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AIR POLLUTION ASPECTS OF MANGANESE AND ITS COMPOUNDS

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Bethesda, Maryland

September 1969

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AIR POLLUTION ASPECTS

OF

MANGANESE AND ITS COMPOUNDS

Prepared for the
National Air Pollution Control Administration
Consumer Protection & Environmental Health Service
Department of Health, Education, and Welfare
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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)
Aldehydes (includes acrolein and formaldehyde)
Ammonia
Arsenic and Its Compounds
Asbestos
Barium and Its Compounds
Beryllium and Its Compounds
Biological Aerosols (microorganisms)
Boron and Its Compounds
Cadmium and Its Compounds
Chlorine Gas
Chromium and Its Compounds (includes chromic acid)
Ethylene
Hydrochloric Acid
Hydrogen Sulfide
Iron and Its Compounds
Manganese and Its Compounds
Mercury and Its Compounds
Nickel and Its Compounds
Odorous Compounds
Organic Carcinogens
Pesticides
Phosphorus and Its Compounds
Radioactive Substances
Selenium and Its Compounds
Vanadium and Its Compounds
Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

This series of reports was compiled and prepared by the Litton personnel listed below:

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ABSTRACT

Inhalation of manganese or its compounds may induce chronic manganese poisoning (a disease of the central nervous system) or manganic pneumonia (a croupous pneumonia). Chronic poisoning is disabling, and manganic pneumonia often results in death. Two studies, one in Norway and one in Italy, have demonstrated the health hazards of manganese air pollution. In addition, manganese compounds are known to act as catalysts in the oxidation of some air pollutants, producing even more undesirable pollutants. They cause generalized soiling of materials, but no evidence of damage to plants is known.

The production of ferromanganese compounds in blast furnaces provides the most common source of manganese air pollution. Other sources include the use of organic manganese fuel additives, welding rods, and incineration of manganese-containing products. During 1964 the average concentration of manganese in the air was 0.10 $\mu g/m^3$; the maximum value recorded was 10 $\mu g/m^3$. Manganese emissions are controlled by normal particulate control methods. No information has been found on the economic costs of manganese air pollution or on the costs of its abatement. Procedures exist for the measurement of this material in the atmosphere; however, discrimination between the various compounds is not made.

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1. INTRODUCTION

Although manganese (Mn) is one of the elements essential to the human body, a high atmospheric concentration may result in (1) chronic manganic poisoning, a disease of the central nervous system,[61] (2) manganic pneumonia,[61] or (3) catalytic oxidation[16,59] of other air pollutants to more undesirable compounds.

Air pollution by manganese arises almost entirely from the manganese and steel industries.[61] Fumes from welding rods and organic manganese compounds may also contribute to air pollution.[10,11,29,46] The organic compounds that have been tested as additives in gasoline, fuel oil, and diesel oil for use in both internal combustion engines and turbine engines may become a source of pollution.

From an air pollution standpoint, the oxides of manganese are the most important of the manganese compounds.[61] Almost all of the manganese in the atmosphere enters it as manganese oxides, such as MnO, Mn_2O_3, or Mn_3O_4. However, these oxides may rapidly react with other pollutants—for example sulfur dioxide and nitrogen dioxide—to form water soluble manganese compounds.

2. EFFECTS

Manganese can exist in 8 different oxidation states (0, +1, +2, +3, +4, +5, +6, +7), of which the bivalent form (Mn^{+2}) is the most stable. Elemental manganese is a highly reactive metal. The lower oxidation states are usually in the form of cations (e.g., Mn^{+2}, Mn^{+3}, Mn^{+4}), while the higher oxidation states form anions (e.g., MnO_3^{-2}, MnO_4^{-2}, MnO_4^{-1}).

The toxicity of manganese compounds appears to depend upon the type of manganese ion present and the oxidation state of the manganese. It has been suggested that manganese cations are more toxic than the anion forms.[61] The permanganate anions, though strong oxidizing agents which show some caustic action, are relatively less toxic than the cations. The bivalent cation is said to be 2.5 to 3 times more toxic than the trivalent cation. Levina and Rabachevsky[38] reported that while manganese oxides such as MnO, Mn_3O_4, Mn_2O_3, and MnO_2 were toxic to rats, the higher oxides were the most toxic.

The associated anion is reported to affect the toxicity of manganese: manganese citrate is more lethal than manganese chloride.[61] See Table 1 in the Appendix for the properties, toxicity, and uses of some manganese compounds.

2.1 Effects on Humans

Exposure to manganese in the air may result in chronic

manganese poisoning and/or manganic pneumonia.

2.1.1 Chronic Manganese Poisoning

Chronic manganese poisoning is primarily a disease of the central nervous system, resulting in total disablement after exposure to high concentrations of manganese dust (usually the oxides) for only a few months. The disease is reversible if it is recognized early and the person is removed from exposure to the dust. Symptoms include a peculiar slapping gait, weakness in doing heavy work, cramps or tremors of the body and extremities, a mask-like expression, impulsive and uncontrollable laughter, speech difficulty, hallucinations, insomnia, absentmindedness, and mental confusion.[12,25,27,39,47,66]

Manganese may be absorbed by inhalation, by ingestion, or through the skin; most damage results from prolonged inhalation. High concentrations of manganese are found in the hair.[10,11,29] Radioactive manganese-54 has been used as a tracer to study the pathology of manganese poisoning.[19,42]

Manganese is primarily excreted in the feces.[35] Studies comparing excretion rates in healthy manganese workers and in persons suffering from chronic manganese poisoning reveal that healthy workers have a higher-than-normal manganese excretion rate and persons suffering from manganese poisoning have a lower-than-normal manganese excretion rate. These results indicate that the retention of manganese in the body varies

with individuals.[48,65] There is evidence that sensitivity to manganese poisoning can develop, since persons who have recovered from the disease appear to be prone to contract it again.[65]

The manganese oxides have been observed to produce chronic poisoning. No information has been found on the effects of other compounds of manganese.

Wasserman and Mihail[65] have summarized (Table 2, Appendix) the prevalence of chronic manganese poisoning among manganese miners. They have also suggested that manganese workers often suffer from manganoconiosis. Of 820 miners, 209 were suspected of having manganoconiosis as determined by X-ray.

The average dose of manganese which causes illness has not been determined. However, miners working with pneumatic drills in Chilean manganese mines in an atmosphere of approximately 5,000 particles per cubic meter (less than 10 μ* diameter) developed manganism in 49 to 480 days, the average time being 178 days.[65]

The disease is controlled mainly by removing the patient from the dusty environment. In some cases, administration of calcium disodium ethylenediamine tetracetic acid has increased the excretion rate (primarily in the urine).[61]

2.1.2 Manganic Pneumonia

Manganic pneumonia, often referred to as a croupous pneumonia, is distinguished by the following symptoms: a sudden

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* μ: micron(s).

onset of pneumonia, intense dyspnea, high temperature, radiological signs of acute lobar pneumonia, and little expectoration (often hemorrhagic). Manganic pneumonia does not respond to antibiotics and is accompanied by a high mortality rate--four times higher than that for lobar pneumonia.[24]

Elstad[28] reported on conditions which he noted in the small town of Saude located on the Western shore of Norway. Until 1932 the town was frequented by tourists. In that year, a plant built in the town to manufacture manganese alloys began discharging clouds of dark brown smoke into the atmosphere. This ended the inflow of tourists into that town, and gave Saude a reputation as a high morbidity center due to the frequent occurrence of croupous pneumonia resulting in a high mortality rate. Data presented by Elstad indicated that the total mortality in Norway from all causes was the same as in Saude, amounting correspondingly to 10.7 and 10.1 per 1,000 persons, but mortality due to croupous pneumonia was 8 times higher in Saude than for Norway in general: 3.27 as compared with 0.4 per thousand persons. In 1924 to 1935 deaths caused by croupous pneumonia accounted for 3.65 percent of Norway's total mortality, while in Saude it was 32.2 percent or nearly 10 times as high. Postmortem examinations indicated that the manganese concentration in lung tissues of persons who died of croupous pneumonia was considerably higher than normal.

The high morbidity and mortality caused by croupous pneumonia in Saude was regarded by Elstad as the result of systematic manganese discharge into the atmosphere by the manganese plant. Examination showed that the ventilation system of the electric smelting furnace was adequate insofar as the working premises were concerned, but the smoke containing manganese compounds was discharged into the atmosphere close to the metallurgical plant. However, at 3 km from the discharge point manganese concentrations in the air were high, and the particle diameters were 5μ or greater. During windy seasons the smoke was dispersed in a short time, but during periods of calm or fog, the valley in which the town of Saude was located was covered with a continuous cloud of smoke. Elstad noted that the rise in morbidity caused by croupous pneumonia and its consequent mortality paralleled the increase in the amount of ferromanganese discharged by the plant. This, according to Elstad, served as additional evidence of the causal relationship between the plant's discharges and the local high frequency of morbidity and mortality caused by croupous pneumonia.

Surveys[26] made in the U.S.S.R. of 1,200 residents indicated that 95.6 percent of the persons interrogated within a 500-m zone complained of unfavorable effects of the plant discharges. Residents within the 500-m zone complained of high dust density. For example, when the wind blew from the plant toward the residential area, house windows had to be closed;

clothes could not be hung to dry in the open air; snow became covered with a layer of black dust; and more frequent housecleaning became necessary. Morbidity studies established that among residents of a nearby village, the frequency of nervous system effects was similar to the frequency of these effects among the adult population of the industrial town. No evidence of neurointoxication was found in workers.

Analysis of nasal mucosa smears made of 700 children, mostly of preschool age, showed the presence of manganese in 62 percent of the cases, frequently amounting to 95 µg. The water in which the children washed their hands was found to contain 38,800 µg of manganese per square meter of skin area. These studies also revealed that 34.3 to 48.1 percent of the children examined suffered from ear, nose, and throat problems. Neuropathologic studies were made of 204 children; findings, positive in 16 children only, were represented by light asthenia, vertigo, neurosis, and vegetative syndrome. Roentgenological examinations disclosed pulmonary changes in 75 percent of the children, and many of these changes were tuberculous. Other changes were periobronchitis of differing degrees, and periovascularitis, thought by the roentgenologist to be the result of past diseases, especially in repeat cases. Thus, results obtained in the study of morbidity among children of the plant village indicated unfavorable shifts in the children's health. The role played by manganese and in particular by

ferromanganic dust in the etiology of such tissue diseases as inflammatory processes of the respiratory passages and sclerotic lung changes was established with more certainty through animal experiments. However, such manganese concentrations were tens and hundreds of times greater than the manganese concentration allowable in working areas.

A similar situation was reported by Pancheri,[51] who attributed the increased frequency of pneumonia in Aosta, Italy, to a metallurgical plant emitting manganese dust.

Davies[22] observed a high rate (26/1,000 miners) of pneumonia in manganese workers, and attempted to support the supposition that manganese produced the pneumonia by means of experiments on mice. He concluded that mice show "an increased susceptibility to pneumococci or streptococci" and "in man and animals, manganese dust in suitable particle size introduced into the respiratory system will, without the presence of other factors, cause pneumonitis."[23] Dust concentrations of 1,000 to 8,000 particles per cubic meter containing 2,000 to 17,000 $\mu g/m^3$ of manganese dioxide were encountered by the workers studied, yet no cases of chronic poisoning were observed.

Van Beukering[63] also reported a higher rate of pneumonia among manganese miners of South Africa than in a control group of iron miners. These results are compared with those of Davies in Table 3 in the Appendix. Again, no cases of chronic poisoning were observed.

Some of the early studies on manganic pneumonia are listed in Table 4 in the Appendix. The theory that manganese causes a disease--manganic pneumonia--rests on statistical studies which provide evidence of the abnormally high percentage of pulmonary illnesses in the various sectors of the manganese industry. However, the thesis that manganese can produce manganic pneumonia is not without opposition. Heine,[33] unable to produce manganic pneumonia in animal experiments, has reviewed the literature and proposed that all cases of pneumonia can be explained by "droughts, long-term unemployment, undernourishment, weather conditions, etc." Moreover, he claims that there is no increased susceptibility to infection. In addition, Stocks[60] has attempted to correlate pneumonia with the presence of trace elements in 23 British cities. His findings show a correlation between pneumonia and beryllium, but no correlation of pneumonia with manganese. However, this lack of correlation may be due to the concentration factor. The concentrations are quite low, ranging from 0.005 to 0.130 $\mu g/m^3$, with most cities having less than 0.050 $\mu g/m^3$.

All of these findings are based on results of inhalation of ferromanganese dust or manganese oxides. Some experimental work with animals shows that similar pulmonary effects occur with other manganese compounds, such as manganous chloride. Rats separately injected intratracheally with manganese dioxide and manganous chloride showed histological changes in the lungs, discharge of mucus in the epithelial cells of the bronchi,

ragged epithelium, and loosened cells from the basal membrane.[61] However, the effect of inhaling low concentrations of various manganese compounds over a long period has not been determined.

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No information has been found in the literature on the effects of manganese air pollution on wild or domestic animals. Manganese is often added to the feed of animals, especially chickens, to prevent manganese deficiency.[27]

2.2.2 Experimental Animals

Studies with rabbits,[22] mice,[33] and rats show that these animals suffer the same types of symptoms as humans.[9]

Joetten[36] exposed rabbits to manganese in a ferromanganese metallurgical plant. All of these rabbits later died of pneumonia either before or after intranasal inoculation with pneumococci. However, all the control animals inoculated with pneumococci survived.

Heine[33] demonstrated that various forms of manganese proved toxic to mice: manganese dust (95% Mn), ferromanganese (88-90% Mn), blast furnace manganese (75% Mn), manganese dioxide (66% Mn), manganese silicon (60% Mn), manganese ore (50% Mn), vanadium slag (29.5% Mn as MnO), and Thomas meal (6.7% Mn as MnO). The degree of toxicity of the various substances was a function of the manganese content rather than the oxidation state of the manganese. From a series of experiments on both mice and guinea pigs he concluded that metallic manganese can be absorbed through the lungs, skin, and gastrointestinal tract. There was

an increase of manganese in the liver following inhalation of manganese. In the case of absorption through the skin, there was an increase of manganese in the liver, muscles, and bones. After ingestion, high manganese levels were found in the brain.

2.3 Effects on Plants

No information has been found on the effects of air pollution on plants. Manganese is known to be essential to higher plants,[64] and for this reason manganese salts and oxides are used as fertilizers.[58]

2.4 Effects on Materials

Manganese and its compounds are active chemicals which either react with materials or catalyze other reactions.[58] Their effect on catalytic oxidation appears to be of prime importance in relation to air pollution. However, soiling has been a common complaint near ferromanganese plants.

Sulfur dioxide and nitrogen dioxide react readily with manganese dioxide to produce soluble sulfates, dithionates, and nitrates[58] by the following reactions:

$$MnO_2 + SO_2 \rightarrow MnSO_4$$

$$2MnO_2 + 3SO_2 \rightarrow MnS_2O_6 + MnSO_4$$

$$MnO_2 + 2NO_2 \rightarrow Mn(NO_3)_2$$

These reactions have been utilized to remove sulfur dioxide from flue gases.[14,15,53] But more important is the fact that small amounts of manganese, usually as manganese

sulfate formed in the reaction of manganese dioxide with sulfur dioxide, will catalyze the oxidation of sulfur dioxide to sulfur trioxide.[20]

$$2H_2SO_3 + O_2 \xrightarrow{MnSO_4} 2H_2SO_4$$

Laboratory studies of this reaction showed that the reaction rate became so rapid when the catalyst concentration was increased above 15 ppm that it was necessary to design a flow apparatus to measure the rates. Bracewell and Gall[16] have shown that these reactions will take place in fog. Assuming a water concentration of 200,000 $\mu g/m^3$ in the air and a manganese concentration of 0.2 $\mu g/m^3$ in a solution, a sulfur dioxide concentration of 1,750 $\mu g/m^3$ would result in a rate of conversion to sulfuric acid of about 25 $\mu g/m^3$ per hour. The rate of reaction increases with the increase in the manganese concentration: the rate is tripled each time the manganese concentration is doubled. The rate also increases linearly with the increase in sulfur dioxide concentration. While other materials such as platinum, graphite, charcoal, vanadium(V) oxide, chromium(III) oxide, ferric oxide, and nitrogen oxides will catalyze the oxidation of sulfur dioxide to sulfur trioxide, manganese sulfate was found to be the most active.[5] The manganese concentration in the atmosphere of most cities is sufficient to catalyze the oxidation. In view of the above reactions, it may be impossible to find manganese oxides in the air since they react readily to form sulfates and nitrates.

Catalytic oxidation of hydrocarbons may also take place. However, very little information was found in the literature on this subject. Hopcalite, a manganese and copper oxide catalyst, has been used to catalyze oxidation of hydrocarbons in flue gases and automobile exhausts.[18,59] Normally, these oxidations take place at high temperatures (100° to 600°C).

Organic catalysts containing methylcyclopentadienyl manganese tricarbonyl have been marketed by the Ethyl Corporation. These catalysts burn and form manganese oxides which promote combustion of organic fuels, including tiny particles of carbon, and increase the octane rating of the fuel.[29,58]

2.5 Environmental Air Standards

The industrial threshold limit value (8-hour) for manganese for those occupationally exposed was originally recommended by the American Conference of Governmental Industrial Hygienists as 6,000 $\mu g/m^3$. This has since been reduced[62] to 5,000 $\mu g/m^3$. The latter value was also recommended by the American Industrial Hygiene Association.[35] The U.S.S.R.[50,54] has recommended a 24-hour limit of 10 $\mu g/m^3$ for manganese and its compounds. The maximum allowable one-time concentration is 30 $\mu g/m^3$.

3. SOURCES

Manganese compounds in the atmosphere are generated primarily by metallurgical uses in the iron and steel industry, organomanganese additives for fuels, and possibly incineration of manganese products or manganese-containing products.[30,45]

These sources all provide oxidizing atmospheres in which manganese may be oxidized in a variety of ways. When heated in air the following reactions[58,63] will take place:

$$4MnO_2 \xrightarrow{307^{\circ}-600^{\circ}C} 2Mn_2O_3 + O_2$$

$$6Mn_2O_3 \xrightarrow{800^{\circ}-1200^{\circ}C} 4Mn_3O_4 + O_2$$

$$4Mn + 3O_2 \xrightarrow{\text{Heated in Air}} 2Mn_2O_3$$

$$6MnO + O_2 \xrightarrow{\text{Heated in Air}} 2Mn_3O_4$$

Thus, most manganese emissions to the atmosphere are in the form of oxides. However, in the presence of sulfur dioxide and nitrogen dioxide, these oxides are rapidly converted to sulfates and nitrates (see Section 2.4).

3.1 Natural Occurrences

Manganese is widely distributed in the combined state, ranking 12th in abundance (1,000 µg/g) among the elements in the earth's crust. It is commonly found associated with iron ores in concentrations too low in most cases to make its commercial recovery attractive. The most common manganese minerals are:

Pyrolusite	MnO_2 (black)	60-63% Mn
Psilomelane	$BaMnMn_8O_{16}(OH)_4$ (black)	45-60% Mn
Hausmannite	Mn_3O_4 (brown)	72% Mn
Rhodocrosite	$MnCl_3$ (light rose)	47% Mn
Rhodonite	$MnSiO_3$ (reddish brown)	42% Mn
Braunite	$3Mn_2O_3 \cdot MnSiO_3$ (black)	63% Mn

Ores containing less than 40 percent of manganese are usually not suitable for metallurgical purposes.

The manganese mining industry in the United States does not contribute significantly to air pollution. Only 1 to 2 percent of the total manganese ore processed in this country is domestically mined[14] (see Table 5 in the Appendix). The States of Montana, New Mexico, and Minnesota have manganese-producing mines.[44,45,58] Table 6 in the Appendix shows the manganese ore resources in the United States.

3.2 Production Sources

3.2.1 Iron and Steel Industry

Most of the manganese imports are in the form of manganese ores, over 90 percent of which are used in the iron and steel industry.[45] Therefore, the smelting and refining of the ore represent the largest potential pollution sources in the United States. The capacity of steel blast furnaces and the location of ferromanganese furnaces are given in Tables 7 and 8 in the Appendix, and emission rates are given

in Table 9 in the Appendix.

3.2.1.1 Ferromanganese Blast Furnaces

Although the number of furnaces producing ferromanganese is small, the process which they use, if uncontrolled, could produce more pollution than any of the other metallurgical processes.[55] Uncontrolled emissions in 1951 produced as much as 8,200,000 to 15,500,000 $\mu g/m^3$ of exhaust gas, with an average of 13,700,000 $\mu g/m^3$. The emissions from two 350-ton ferromanganese furnaces averaged 16,500,000 $\mu g/m^3$ in a gas volume of 3,920 m^3/min resulting in approximately 142 tons of dust per day containing 21 to 36 tons of manganese. This suggests that approximately 0.03 to 0.05 tons of manganese per ton of ore could be emitted. The ferromanganese blast furnace production was 651,987 tons in the United States in 1966.[45] This source could contribute from 19,500 to 32,500 tons of manganese to the atmosphere each year.

The particulates from a ferromanganese furnace are extremely small, with 80 percent ranging in size from 0.1 to 1 μ. These particulates contain:

15-25% manganese

0.3-0.5% iron

8-15% sodium and potassium oxides

9-19% silica

3-11% alumina

8-15% calcium oxide

4-6% magnesium oxide

5-7% sulfur

1-2% carbon

3.2.1.2 Electric-Arc Furnaces

Dust and fume emissions from an electric-arc furnace average approximately 10.6 lb/ton of steel melted, the range being from 4.5 to 29.4 lb/ton. These particulates contain approximately 4 percent of manganous oxide (MnO) with 70 percent of the particles less than 5 μ in diameter.[55] Manganese emissions from electric-arc furnaces producing ferromanganese may be higher than from those producing steel. Electric-arc furnaces produced 294,223 tons of ferromanganese in 1966.[45]

3.2.1.3 Other Furnaces

Some manganese is found in the particulate material emitted from basic oxygen and open-hearth furnaces. However, these concentrations are relatively low.[55]

3.2.2 Coal

The concentration of manganese in coal ash varies between 0.005 and 1.0 percent, depending on the origin of the coal.[1]

Analyses of particulate emissions from six different types of coal-fired power plants[31,57] showed that the concentration of manganese emitted ranged between 60 and 400 $\mu g/m^3$ as shown in Table 10 in the Appendix.

3.2.3 Fuel Oil

Dust emissions from burning residual fuel oil average about 55,000 $\mu g/m^3$ or approximately 2 g/lb of oil fired.[56] The concentration of manganese dioxide in the particulate is approximately 400 µg/g. This would result in an emission of 800 µg of manganese dioxide per pound of fuel oil burned. A boiler burning 1,000 pounds of oil per hour would be discharging 0.8 g of manganese dioxide into the air per hour.

3.3 Product Sources

Approximately 150,000 tons of manganese ore are used by the chemical industry[45] annually and in the production of dry-cell batteries.

3.3.1 Dry-Cell Batteries

The manufacturing of dry-cell batteries probably does not constitute an air pollution hazard, although approximately 30,000 tons of high-grade manganese ore are used annually in this industry.[45] However, the disposal of old dry-cell batteries by incineration could possibly be a source of manganese air pollution.

3.3.2 Chemicals

Fuel additives represent important manganese chemical products associated with air pollution.[10,11,29,46] These additives fall into two classes, antiknock compounds and smoke inhibitors. Both classes of organic manganese compounds have

been patented and tested by the Ethyl Corporation. The most successful antiknock compound is methylcyclopentadienyl manganese tricarbonyl, which is mixed with tetraethyl lead to increase the octane rating of gasoline. A typical mixture is given in Table 11 in the Appendix. More than 2 ml of this mixture per gallon of gasoline (approximately 36,000 µg/gal of manganese) is recommended. The quantity of this mixture actually used has not been disclosed. However, a large proportion of the manganese chloride produced in the United States goes into the manufacture of these chemicals.[58]

Chemical fertilizers containing manganese ethylene-bis-dithiocarbamate (maneb) are another possible source of manganese air pollution. Approximately 10,000 tons of manganese are used as fertilizers annually.[58]

3.3.3 Other Sources

Numerous studies (see list of other references) concern the use of manganese for the control of sulfur dioxide, mercaptans, and sulfides. This use is primarily in wet scrubbers and probably does not constitute a large source of pollution.

About 10,000 tons of manganese (20,000 to 25,000 tons of manganese dioxide) are used annually in welding rods and fluxes for iron and steel.[58] This causes some local pollution in welding shops, but no information was found regarding urban air pollution from this source.

Permanganates are used in a wide variety of applications, such as in air pollution control for sulfides and mercaptans, odor control in barnyards, and in water treatment.[58] However, the largest quantity is used by the chemical industry. Permanganates also have some applications as bactericides, fungicides, and astringents in greenhouses, fisheries, etc.

Manganese dioxide is used in safety matches and strikers as well as in fireworks and signal flares.[58]

3.4 Environmental Air Concentrations

Air quality data obtained from the National Air Sampling Network[2,4,6,7] are shown in Table 12 in the Appendix. These data show that during 1964 the manganese concentration for the cities studied ranged up to 10 $\mu g/m^3$, the average being 0.10 $\mu g/m^3$. The highest values, up to 10 $\mu g/m^3$, have been recorded in Charleston, W. Va.

4. ABATEMENT

The emission of manganese particulates will be controlled at the same time as the particulates from the steel furnaces and incinerators. No special equipment is required to remove manganese. However, the ferromanganese furnace presents special problems.[17,55]

Control of manganese from steel furnaces is accomplished by various types of collectors, including electrostatic precipitators, high-efficiency wet scrubbers, and fabric filters.[13,21] Four physical factors make the dust collection economically difficult: the small particle size (as low as 0.03 μ), the large volume of gas, the high gas temperature, and the low value of the recovered material.

Control of emissions from a ferromanganese blast furnace is more difficult than from other furnaces because the waste gas temperature is hotter and the dust is finer. Electrostatic precipitators have been successful in removing approximately 80 to 90 percent of the dust. No economical way of using the collected dust has been developed.[55]

Control of emissions from burning fuels containing antiknock and smoke-inhibiting additives may require special systems. The hazards of these organic manganese additives are to be studied as required by the Clean Air Act.[52]

5. ECONOMICS

No information has been found on the economic losses due to manganese air pollution, or on the costs of its abatement.

Data on the production and consumption of manganese are presented in Section 3.

6. METHODS OF ANALYSIS

6.1 Sampling Methods

Dusts and fumes of manganese compounds may be collected by any methods suitable for collection of other dusts and fumes; the impinger, electrostatic precipitator, and filters are commonly used.[3,27]

6.2 Quantitative Methods

Many methods of analysis have been used for the determination of manganese. In several methods, such as atomic absorption, emission spectrography, and neutron activation, the chemical species does not matter. The essential requirement is a representative sample in the activation site. With atomic absorption, all of the manganese analyzed must be in solution or suspension.[32,34,37,40,67]

With chemical methods, care must be taken to insure that the manganese is not only in solution, but also in a single oxidation state. The most common method of determining manganese in air samples is a colorimetric method. In this procedure, the manganese is oxidized to permanganate by periodate ions. The color of the permanganate ion is very intense and follows Beer's law over a large range. A 0.5-ft^3 sample collected in a midget impinger is sufficient to determine manganese at a 5,000 $\mu g/m^3$ concentration.[40]

The following sensitivities are listed for the different analytical methods:

Method	Sensitivity (μg/g)
Colorimetric permanganate method	0.1
Emission spectrography[a,b]	10-1,000
Neutron activation[a,b]	0.001-1
Atomic absorption[a,b]	0.01-20
Flame photometry[a,b]	0.1-500

The emission spectrographic method is used to analyze samples collected by the National Air Sampling Network. Working standards are made by diluting a solution containing 20 μg/0.05 ml by 1/2, 1/4, 1/8, ... 1/1024. The minimum concentration detectable by the emission spectrograph is 0.011 for urban air and 0.0060 for nonurban air. The difference in sensitivity is due to different extraction methods used in preparing the sample for emission spectrography.[3,8]

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[a]Sensitivity depends on interfering elements.
[b]These sensitivities were not determined on air samples.

7. SUMMARY AND CONCLUSIONS

Inhalation of manganese oxides may cause chronic manganese poisoning or manganic pneumonia. Chronic manganese poisoning is a disease affecting the central nervous system, resulting in total or partial disability if corrective action is not taken. Some people are more susceptible to manganese poisoning than others. Manganic pneumonia is a croupous pneumonia often resulting in death. The effect of long exposure to low concentrations of manganese compounds has not been determined.

Manganese compounds are known to catalyze the oxidation of other pollutants, such as sulfur dioxide, to more undesirable pollutants--sulfur trioxide, for example. Manganese compounds may also soil materials.

The most likely sources of manganese air pollution are the iron and steel industries producing ferromanganese. Two studies, one in Norway and one in Italy, have shown that the emissions from ferromanganese plants can significantly affect the health of the population of a community. Other possible sources of manganese air pollution are manganese fuel additives, emissions from welding rods, and incineration of manganese-containing products, particularly dry-cell batteries. Manganese may be controlled along with the particulates from these sources. Air quality data in the United States showed that the manganese concentration averaged 0.10 $\mu g/m^3$ and ranged as high as 10 $\mu g/m^3$ in 1964.

No information was found on the economic costs of manganese air pollution or on the costs of its abatement.

Based on the material presented in this report, further studies in the following areas are suggested:

(1) The effect of inhalation over varying periods of time of low concentrations of the manganese compounds found in the atmosphere.

(2) The chemical composition and particle-size distribution of the manganese compounds in the atmosphere.

(3) The effect of manganese air pollution on commercial plants and animals.

(4) Measurement of the concentration of manganese both near suspected sources and as emitted from suspected sources.

(5) The economic losses due to manganese air pollution.

REFERENCES

1. Abernethy, F. R., and F. H. Gibson, Rare Elements in Coal, Bureau of Mines, Information Circular No. 8163 (1963).

2. Air Pollution Measurements of the National Air Sampling Network, 1953-1957, U.S. Dept. of Health, Education and Welfare, Public Health Service, Cincinnati, Ohio (1958).

3. Air Pollution Measurements of the National Air Sampling Network, Analyses of Suspended Particulates, 1957-1961, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 978, U.S. Government Printing Office, Washington D.C. (1962).

4. Air Pollution Measurements of the National Air Sampling Network—Analyses of Suspended Particulates, 1963, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio (1965).

5. Air Quality Criteria for Sulfur Oxides, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 1619, U.S. Government Printing Office, Washington, D.C. (1967).

6. Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1964-1965, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio (1966).

7. Air Quality Data, 1962, National Air Sampling Network, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Cincinnati, Ohio.

8. Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966 ed., U.S. Dept. of Health, Education, and Welfare, National Air Pollution Control Administration Publication No. APTD 68-9, U.S. Government Printing Office, Washington, D.C. (1968).

9. Altman, P. S., et al. Environmental Biology, AD-646890, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio (Nov. 1966).

10. Arkhipova, O. G., M. S. Tolgskaya, and T. A. Kochetkova, Toxic Properties of Manganese Cyclopentadienyltricarbonyl Antiknock Substance, Translated by B. S. Levine, U.S.S.R. Literature on Air Pollution and Related Occupational Disease 12:85 (1963).

11. Arkhipova, O. G., M. S. Tolgskaya, and T. A. Kochetkova, Toxicity Within a Factory of the Vapor of New Antiknock Compound, Manganese Cyclopentadienl-tricarbonal, Hyg. Sanitation 30(4):40 (1965).

12. Balani, S. G., C. M. Umarji, R. A. Bellare, and H. C. Merchant, Chronic Manganese Poisoning—A Case Report, J. Postgraduate Med. 13:116 (1967).

13. Benz, D. L., and R. Bird, Control of Pollution from Electric Arc Furnaces at Oregon Steel Mills Co. Preprint. Oregon Steel Mills Co., Portland, Oreg. (1965).

14. Bienstock, D., L. W. Brunn, E. M. Murphy, and H. E. Benson, Sulfur Dioxide—Its Chemistry and Removal from Industrial Waste Gases, Bureau of Mines, Information Circular No. 7836 (1958).

15. Bienstock, D., and F. J. Field, Bench-Scale Investigation on Removing Sulfur Dioxide from Flue Gases, J. Air Pollution Control Assoc. 10(2):121 (April 1960).

16. Bracewell, J. M., and D. Gall, "The Catalytic Oxidation of Sulfur Dioxide in Solution at Concentrations Occurring in Fog Droplets," in Air Pollution, Proceedings of the Symposium on the Physico-Chemical Transformation of Sulphur Compounds in the Atmosphere and the Formation of Acid Smogs, Mainz, Germany, June 8-9, 1967, Organisation for Economic Co-operation and Development Directorate for Scientific Affairs (1967).

17. Brandt, A. D., Current Status and Future Prospects—Steel Industry Air Pollution Control, Presented at National Conference on Air Pollution, Washington, D.C. (Dec. 12-14, 1966).

18. Christian, J. G., and J. E. Johnson, Catalytic Combustion of Atmospheric Contaminants over Hopcalite, Intern. J. Air Water Pollution 9(1-2):1 (1965).

19. Cotzias, G. C., K. Hoiiuchi, S. Fuenzalida, and I. Mena, Chronic Manganese Poisoning—Clearance of the Issue Manganese Concentrations with Persistence of the Neurological Picture, Neurology (Minn.) 18:376 (1968).

20. Coughanour, D. R., and F. E. Krause, The Reaction of SO_2 and O_2 in Aqueous Solutions of $MnSO_4$ Ind. Eng. Chem. Fundamentals 4(1):61 (1965).

21. Danielson, J. A., Air Pollution Engineering Manual, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 999-AP-40, U.S. Government Printing Office Washington, D.C. (1967).

22. Davies, T. A. L., Manganese Pneumonitis, Brit. J. Ind. Med. 3:111 (1946).

23. Davies, T. A. L., and H. E. Harding, Manganese Pneumonitis, Brit. J. Ind. Med. 6:82 (1949).

24. Dervillee, P., F. Mouchand-Beuchant, J. Charpentier, and E. Dervillee, On Manganic Pneumonia, Arch. Maladies Professionneiles (Arch. Occup. Diseases) 27:222 (1966).

25. Documentation of Threshold Limit Values, American Conference of Governmental Industrial Hygienists, Committee on Threshold Limit Values, Cincinnati, Ohio (1962).

26. Dokuchaev, V. F., and N. N. Skvortsova, Atmospheric Air Pollution with Manganese Compounds and Their Effect on the Organism, B. S. Levine (Translator), U.S.S.R. Literature on Air Pollution and Related Occupational Disease 9:40 (1962).

27. Elkins, H. B., The Chemistry of Industrial Toxicology (New York: Wiley, 1959).

28. Elstad, D., Manganholdig Fabrikkrvek som Medvirkende Arsak ved Pneumoni-Epidermier i en Industribygd, Nord. Med. 3:2527 (1939).

29. Gas Turbine Fuel Additive, Diesel and Gas Turbine Progress 33 (12):71 (1967).

30. Gerlach, J., K. Hochgeschwender, and F. Pawlek, Contributions to the Extraction of Rare Metals from Flue Dusts, Metall. 21(7):700 (July 1967).

31. Gerstle, R. W., S. T. Cuffe, A. A. Orning, and C. H. Schwartz, Air Pollutant Emissions from Coal Fired Power Plants. Report No. 2, J. Air Pollution Control Assoc. 15(2):59 (1956).

32. Gordon, C. M., and R. E. Larson, Activation Analysis of Aerosols, NRL Quarterly on Nuclear Science and Technology, Naval Research Lab., Washington, D.C., Jan. 1, 1964, pp.17-22.

33. Heine, W., Observations and Experimental Investigation of Manganese Poisonings and Manganese Pneumonia, Z. Hyg. Infektions-Kraukuten (J. Hyg. Infect. Diseases) 125:1 (1944).

34. Horwitz, W. (Ed.), Official Methods of Analysis of the Association of Official Agricultural Chemists, 10th Ed., Association of Official Agricultural Chemists, Washington, D.C. (1965).

35. Hygienic Guide Series: Manganese and Its Inorganic Compounds, Am. Ind. Hyg. Assoc. J. 24:284 (1963).

36. Joetten, K. W., The Use of Animal Experiments for the Detection and Prevention of Lung Damage by Occupational Dusts, Arch. Hyg. Bakteriol. (Arch. Hyg. Bact.) 131:222 (1944).

37. Kolthoff, T. M., P. J. Elving, and E. B. Sandell, Treatise on Analytical Chemistry, Part II—Analytical Chemistry of the Elements, vol. 7, S, Se-Te, F Halogens, Mn, Re (New York: Interscience, 1961).

38. Levina, E. N., and E. G. Rabachevsky, Changes in Lung Tissue with Intratracheal Injection of Manganese, Gigiena i Sanit. 1:25 (1955).

39. Mahoney, J. P., and W. J. Small, Studies on Manganese—III, The Biological Half-Life of Radiomanganese in Man and Factors Which Affect This Half-Life, J. Clin. Invest. 47:643 (1968).

40. Manual of Analytical Methods—Determination of Manganese in Air, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio (1958).

41. Markwith, R. D., Manganese, Office Department of Health, Division of Adult Hygiene (1940).

42. Mena, I., O. Marin, S. Fuenzalida, and G. C. Cotzias, Chronic Manganese Poisoning—Clinical Picture and Manganese Turnover, Neurology (Minn.) 17:128 (1967).

43. The Merck Index, 8th ed. (Rahway, N.J: Merck, 1968).

44. Mineral Facts and Problems, Bureau of Mines Bulletin 630, U.S. Government Printing Office, Washington, D. C. (1965).

45. Minerals Yearbook, Bureau of Mines, U.S. Government Printing Office, Washington, D.C., 1948-1966.

46. Motor Vehicles, Air Pollution, and Health, A Report of the Surgeon General to the U.S. Congress in Compliance with Public Law 86-493, The Schenck Act, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Division of Air Pollution, House Document No. 489, U.S. Government Printing Office, Washington, D.C., p. 274 (1962).

47. Nabi, S. E. D. A., and K. S. Kayed, EMG and Conduction Velocity Studies in Chronic Manganese Poisoning, Acta Neurol. Scandinav. 41:159 (1965).

48. Naby, S. A. E., and M. Hassanien, Neuropsychiatric Manifestations of Chronic Manganese Poisoning, J. Neurol. Neurosurg. Psychiat. 28:282 (1965).

49. New York—New Jersey, Air Pollution Abatement Activity, Particulate Matter, Phase II, Pre-Conference Investigations, U.S. Dept. of Health, Education, and Welfare, Public Health Service, National Center for Air Pollution Control (Dec. 1967).

50. Nikolaeva, T., Maximum Permissible Concentrations of Harmful Substances in Atmospheric Air of Populated Places, Approved by the Chief Sanitary Inspector of the U.S.S.R., No. YM2-63 (June 20, 1963).

51. Pancheri, G., Industrial Atmospheric Pollution in Italy, in Problems and Control of Air Pollution, F. S. Mallette, Ed. (New York: Reinhold, p. 263, 1955).

52. Personal communication from B. Steigerwald, National Air Pollution Control Administration (Jan. 1969).

53. Pretorius, S. T., and W. G. Mandersloot, The Removal of Air Pollutants from Gases by Reaction with Particulate Solids, Powder Technology 1:129 (1967).

54. Rossano, A. T., Jr., Analysis and Comparison of Available Data on Air Quality Criteria in Member Countries, Inter-Regional Symposium on Criteria for Air Quality and Methods of Measurement, Geneva (Aug. 6-12, 1963).

55. Schueneman, J., M. D. High, and W. E. Bye, Air Pollution Aspects of Iron and Steel Industry, U.S. Dept. of Health, Education, and Welfare, Public Health Service, Publication No. 999-AP-1 (1963).

56. Smith, W. S., Atmospheric Emissions from Fuel Oil Combustion—An Inventory Guide, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 999-AP-2 (1962).

57. Smith, W. S., and C. W. Gruber, Atmospheric Emissions from Coal Combustion—An Inventory Guide, U.S. Dept. of Health, Education, and Welfare, Public Health Service Publication No. 999-AP-24 (1966).

58. Standen, A. (Ed.), "Manganese and Manganese Compounds," in Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed. (New York: Interscience, 1967).

59. Stein, K. C., J. J. Feeman, G. P. Thompson, J. F. Shultz, L. J. E. Hofer, and R. B. Anderson, Catalytic Oxidation of Hydrocarbons Ind. Eng. Chem. 52:671 (1960).

60. Stocks, P., On the Relationship Between Atmospheric Pollution in Urban and Rural Localities and Mortality from Cancer Bronchitis and Pneumonia, with Particular Reference to 3,4-Benzpyrene, Beryllium, Molybdenum, Vanadium and Arsenic, Brit J. Cancer 14:397 (1960).

61. Stokinger, H. E., "Manganese," in Industrial Hygiene and Toxicology, vol. II, 2nd ed., F. A. Patty, Ed. (New York: Interscience, 1963).

62. Threshold Limit Values for 1967, Adopted at the Annual Meeting of the American Conference of Governmental Industrial Hygienists, Chicago, Ill. (May 1-2, 1967).

63. Van Beukering, J. A., The Occurrence of Pneumonia Among Miners in an Iron Mine and a Manganese Ore Mine in South Africa, Dutch Med. J. 110(10):473 (1966).

64. Warren, H. V., Medical Geology and Geography, Science 148 (3669):534 (1965).

65. Wasserman, M., and G. Mihail, Significant Indicators for the Early Detection of Manganism in Miners Working in Manganese Mines, Acta Medicinae Legalis et Socialis (Liege) 17:61 (1964).

66. Whitlock, C. M., Jr., S. J. Amuso, and J. B. Bittenbender, Chronic Neurological Disease in Two Manganese Steel Workers, Am. Ind. Hyg. Assoc. J. 27:454 (1966).

67. Willard, H. H., L. L. Merritt, Jr., and J. A. Dean, Instrumental Methods of Analysis, 4th ed. (Princeton, N.J: Van Nostrand, 1965).

OTHER REFERENCES

Anderson, F. J., and H. S. Posselt, Permanganate Oxidation of Sulfur Compounds—Application to Air Scrubbing, Paper 67-114 of the Annual Meeting of the Air Pollution Control Association (1967).

Belyea, A. R., Manganese Additive Reduces SO_3, Power (Nov. 1966).

Chittawadgi, B. S., and N. R. Dave, Reducing Smoke in Diesel Exhaust Gases, The Indian and Eastern Engineer 109(5): 221 (1967).

Davis, F. F. Jr., Smoke Abatement in Gas Turbine for Industrial Use, Presented at the ASME-IEEE Joint Power Generation Conference, Detroit, Mich. (Sept. 24-28, 1967).

DeCorso, S. M., C. E. Hussey, and M. J. Ambrose, Smokeless Combustion in Oil-Burning Gas Turbines, Presented at the ASME-IEEE Joint Power Generation Conference, Detroit, Mich. (Sept. 24-28, 1967).

Douglas, I. H., Direct Fume Extraction and Collection Applied to a Fifteen Ton Arc Furnace, Fume Arrestment, The Iron and Steel Institute, Special Report 83 (1963).

Emanuel, A. G., Potassium Permanganate Offers New Solution to Air Pollution Control, Air Eng. 7(9): 19 (Sept. 1965).

Finfer, E. Z., Fuel Oil Additives for Controlling Air Contaminant Emissions, J. Air Pollution Control Assoc. 17(1): 43 (1967).

Kuehn, M., and R. Tomingas, Attempts to Prevent the Formation of Pollutants in the Exhaust Gases of Two-Stroke Engines and Diesel Engines by Activating Combustion within the Engine, Staub. 25(3): 2 (1965).

Pabbix, G. W., Thermodynamic Evaluation of Basic Oxygen Furnace—Hot Model Studies, Presented at the AIME Annual Meeting, New York (1966).

Posselt, H. S., and A. H. Reidies, Odor Abatement with Potassium Permanganate Solutions, Division of Water, Air and Waste Chemistry, 148th Meeting, American Chemical Society, Chicago, Ill. (Sept. 1964).

Schneider, R. L., Engineering, Operation and Maintenance of Electrostatic Precipitators on Open Hearth Furnaces, J. Air Pollution Control Assoc. 13(8): 348 (1963).

Sem, M. O., and F. C. Collins, Fume Problems in Smelting and Contributions to their Solution, J. Air Pollution Control Assoc. 5(3): 157 (1955).

Shayeson, M. W., Reduction of Jet Engine Exhaust Smoke with Fuel Additives, Paper 670866 for Aeronautic and Space Engineering and Manufacturing Meeting, Los Angeles, Calif. (Oct. 2-6, 1967).

Stein, K. C., J. J. Feeman, and L. J. E. Hofer, Catalytic Oxidation of Hydrocarbons, Bureau of Mines Bulletin 608, Washington, D. C. (1962).

Taylor, W. G., Smoke Elimination in Gas Turbines Burning Distillate Oil, Presented at the ASME-IEEE Joint Power Generation Conference, Detroit, Mich. (Sept. 24-28, 1967).

APPENDIX

APPENDIX

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS[43]

Compound	Properties	Toxicity	Uses
Manganese acetate $Mn(C_2H_3O_2)_2 \cdot 4H_2O$	Pale red, transparent crystals. Decomposes at 1.59°C		As mordant in dyeing, in manufacture of bister, as drier for paints and varnishes
Manganese arsenate $MnHAsO_4$	Reddish-white powder	Poison	
Manganese borate $MnB_4O_7 \cdot 8H_2O$	Brownish-white powder. Insoluble in water or alcohol		In drying varnishes and oils, as drier for linseed oil; in leather industry
Manganese bromide $MnBr_2 \cdot 4H_2O$	Rose-red. mp 64°C		
Manganese carbonate $MnCO_3$	White powder. Insoluble in water or alcohol		In pigment "manganese white," as drier for varnishes, in feeds. Med. use: formerly as hematine
Manganese chloride $MnCl_2 \cdot 4H_2O$	Reddish. mp 58°C	Occurs by inhalation of the dust or fumes. Symptoms: languor, sleepiness, weakness, emotional disturbances, spastic gait, paralysis. Picture resembles Parkinsonism LD s.c. in mice: 210 mg/kg	In dyeing (manganese bister), disinfecting, purifying natural gas; as linseed oil drier; in electric batteries

(continued)

APPENDIX

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Manganese difluoride MnF_2	Pink quadratic prisms. mp 856°C		
Manganese dioxide MnO_2	Insoluble in water	See Manganese chloride LD i.v. in rabbits: 45 mg/kg	This mineral is the source of manganese and all its compounds. Largely used in manufacture of manganese steel; as oxidizer; in alkaline batteries (dry cells); for making amethyst glass, decolorizing glass, painting on porcelain. The precipitate is used in electrotechnics, pigments, browning gun barrels; as drier for paints and varnishes; in printing and dyeing textiles
Manganese diselenite $Mn(SeO_3)_2$	Orange-yellow crystalline powder. Decomposed by heat		
Manganese hypophosphite $Mn(H_2PO_2)_2 \cdot H_2O$	Pink. When heated evolves spontaneously flammable phosphine		Med. use: formerly as hematinic
Manganese iodide $MnI_2 \cdot 4H_2O$	Rose-red crystals. Very soluble in water		

(continued)

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$	Pink. mp 25.8°C		
Manganese oleate $Mn(C_{18}H_{33}O_2)_2$	Brown. Insoluble in water		As drier for varnish
Manganese oxalate $MnC_2O_4 \cdot 2H_2O$	White crystalline powder. Decomposes at 150°C		
Manganese oxide Mn_3O_4	Brownish-black powder. Decomposes at 4.7°C		
Manganese phosphate, diabasic $MnHPO_4 \cdot 3H_2O$	Pink powder		
Manganese pyrophosphate $MnP_2O_7 \cdot 3H_2O$	White powder. Insoluble in water		
Manganese selenate $MnSeO_4 \cdot 2H_2O$			
Manganese selenide MnSe	Gray-black cubic crystals		

(continued)

APPENDIX

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Manganese selenite $MnSeO_3 \cdot 2H_2O$	Monoclinic crystals. Decomposes in air		
Manganese sesquioxide MnO_3	Black fine powder. Insoluble in water		
Manganese silicate $MnSiO_3$	Red crystals or yellowish-red powder. Insoluble in water		As color for special glass; for producing red glaze on pottery
Manganese sulfate $MnSO_4 \cdot H_2O$	Pale red. Loses all water at 400-450°C		In dyeing; for red glaze on porcelain, boiling oils for varnishes; in fertilizers for vines, tobacco; in feeds
Manganese sulfide MnS	Pink, green, or brown powder. Practically insoluble in water	See Manganese chloride	
Manganese sulfite $MnSO_3$	Reddish-white crystalline powder		

(continued)

APPENDIX

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Manganese trifluoride MnF_3	Red crystalline mass. Decomposes at 3.54°C. Stable to 600°C		
Methyl-cyclopenta-dienyl manganese tricarbonyl[46] $CH_3C_5H_4Mn(CO)_3$			Used to reduce smoke in gas turbine engines, antiknock additive for gasoline
Potassium permanganate $KMnO_4$	Decomposes at 240°C	Dilute solutions are mildly irritating and high concentrations are caustic	Bleaching resins, waxes, fats, oils, straw, cotton, silk, and other fibers; dyeing wood brown; printing fabrics; washing CO_2 in manufacture of mineral waters; photography; tanning leathers; reagent in analytical and organic chemistry; purifying water. Med. use: topical astringent, antiseptic

APPENDIX

TABLE 1 PROPERTIES, TOXICITY, AND USES OF SOME MANGANESE COMPOUNDS (Continued)

Compound	Properties	Toxicity	Uses
Manganese cyclopentadienyltricarbonyl (MCT)[10,42] $C_5H_5Mn(CO)_3$	Bright yellow crystalline powder. Sublimes at 75-77°C	MCT is toxic in low concentrations and has marked cumulative properties. A concentration of MCT vapor of the order of hundred thousands of $\mu g/m^3$ of air is lethal on a one-time exposure. 10,000 $\mu g/m^3$ caused severe and lethal poisoning when administered repeatedly. MCT concentrations of 1,000 $\mu g/m^3$ affected the nervous system and gave rise to early histological changes in the respiratory tract. The new antiknock compound acts as a mild irritant at the site of application but does not penetrate the skin when in oil and gasoline solution. The toxicity of MCT is enhanced by the solvent tetrahydrofuran used in its manufacture. MCT solutions in this solvent penetrate the intact skin and give rise to poisoning	Antiknock compound for internal combustion engines

TABLE 2[26]

PREVALENCE OF MANGANISM IN MINERS WORKING IN MANGANESE MINES

Location of Mines	Year of Survey or Publication of Studies	No. of Miners Examined	No. of Miners with Manganism	Per-cent	Observations
Germany (Upper Schleswig)	1879		40-50		These mines contain zinc and manganese deposits. A diagnosis of manganism has recently been assigned to the case which Schlokow considered to be one of zinc intoxication
Spain	1935	65	2	3	
Egypt	1936		26		Baader has confirmed the cases of manganism detected by the Egyptian authors; and during the same voyage in Africa, he has detected a few cases of manganism in miners working in the manganese mines of Morocco
Morocco	1936		26		
Germany	1936	44	12		The group of subjects examined consisted of miners who had worked in the mine for more than 10 years. These authors have also described the presence of manganoconiosis and manganic pneumonia in the pathology of miners. This group also included 11 probable cases
Chile	1943		64		
U.S.S.R.	1946		0		Examination of these miners was repeated in 1953 and 1956
Morocco	1949	257	28	10.9	
Rumania	1949-50	576	10		

(continued)

TABLE 2 (Continued)

PREVALENCE OF MANGANISM IN MINERS WORKING IN MANGANESE MINES

Location of Mines	Year of Survey or Publication of Studies	No. of Miners Examined	No. of Miners with Manganism	Per-cent	Observations
Cuba	1952		120		
U.S.S.R.	1953		0		Examination of these miners was repeated in 1956
Italy (Tuscany)	1954		0		The authors explain the absence of manganism by the marked infiltration of water into the mining deposits
Mexico	1954	151	12	7.94	Another case was diagnosed by the same author in a drill operator who worked in another mine
U.S.S.R.	1955-56	972	39	4.01	
U.S.S.R.	1956	170	39		75% of the miners examined have worked in the mine for more than 10 years. These 39 miners exhibited disorders of the central nervous system which ranged from the asthenovegetative syndrome to the extrapyramidal syndrome. 40 other miners displayed disorders of the peripheral nervous system. These authors have also described the presence of manganoconiosis and manganic pneumonia in the pathology of these miners
Chile	1957	83	15		The groups of subjects examined consist of miners who had a high degree of toxic exposure and of those who exhibited clinical disorders for which manganism was suspected

(continued)

TABLE 2 (Continued)

PREVALENCE OF MANGANISM IN MINERS WORKING IN MANGANESE MINES

Location of Mines	Year of Survey or Publication of Studies	No. of Miners Examined	No. of Miners with Manganism	Per-cent	Observations
Morocco	1958	223			158 cases of manganism were found among the drill operators
Morocco	1958	145	9	6.2	
Rumania	1958	827	59	7.13	These authors have also described the presence of manganoconiosis
Japan	1950-59	237			30% of the examined miners suffered from shaking of the body and of the extremities, micrography, disorders of walking or of the coordination of movements, and especially from subjective disorders. During the period of examination (1950-59), the authors noted the gradual worsening of the clinical pictures

APPENDIX

TABLE 3

PNEUMONIA RATE IN MANGANESE WORKERS[64,30]
(Rate/1000 Males)

Year	Manganese Plant	Manganese Mine	Iron Mine	Coal Mine	Boots[23] Health Insurance Society	England and Wales
1938	63				0.52	
1939	50				0.47	1.0
1940	15				0.91	1.2
1941	30				0.59	1.2
1942	24				0.89	1.0
1943	20				1.2	1.2
1944	0				1.0	0.9
1945	26				0.02	0.8
1946	10				0	0.9
1947	30					
1948						
1957-59[64]		26-33		0.8-3.6		
1962[30]		80.8	51			

APPENDIX

TABLE 4. REPORTED PREVALENCE OF CROUPOUS PNEUMONIA AMONG MANGANESE WORKERS [26]

Location of Exposure	Year of Study	No. of Workers Exposed	No. of Workers with Croupous Pneumonia	Percentage of Workers with Croupous Pneumonia	Exposure Time
Manganite mill	1913	10	5	50	27 mo
Norwegian town near ferromanganese plant	1923			32.3	
Mn mine	1923			8.2	
Mn mine	1930		2		
Mn ore shippers	1931	70	37	53	13 yr
Mn mines	1932	442	268	61	
Other mines	1932			11.3	
All industries	1932			3.8	
Mn mines	1932	Most frequent cause of death			
Mn mines	1935	64	6	9.4	
Mn mines	1936	44	23	52*	
Dry-cell factory	1937		1		
Manganite processing plant	1939			5*	
Dry-cell factory		104	14 (11*)	13.5	
Mn mines	1957-59			2.3-3.3	
Coal mines	1957-59			0.08-0.36	
Forest	1957-59			0.78-2.4	

*Workers died of pneumonia.

APPENDIX

TABLE 5

U.S. CONSUMPTION OF MANGANESE ORE AND MANGANESE ALLOYS[45]
(Short Tons)

Type of Consumption	1958	1960	1961	1962	1963	1964	1965	1966
				MANGANESE ORE[a]				
Domestic	45,264	29,080	20,004	24,670	7,135	19,887	24,344	46,159
Foreign	1,452,310	1,917,309	1,697,801	1,840,602	1,834,590	2,221,869	2,848,376	2,323,134
Total[b]	1,497,574	1,946,389	1,717,805	1,865,272	1,841,725	2,241,756	2,872,720	2,369,293
For production of:								
Alloys and metal	1,414,613	1,846,572	1,586,965	1,737,694	1,683,450	2,092,445	2,704,357	2,163,968
Pig iron	5,041	5,805	9,961	14,882	34,830	18,706	27,772	42,941
Chemicals	50,643	65,920	91,470	78,116	94,715	99,670	106,580	128,145
Dry cells	26,604	27,215	28,301	33,625	27,870	30,114	33,865	34,200
				FERROMANGANESE				
Steel ingots	674,495	755,864	778,003	766,673	852,285	967,550	1,040,502	1,048,429

[a] More than 35% Mn.

[b] Includes more than those listed below.

APPENDIX

TABLE 6

MANGANESE ORE RESOURCES OF THE U.S.[58]

Location	Millions of Short Tons	Mn, Avg %
	RESERVES	
Butte, Mont.	5.0	14
Phillipsburg, Mont.	.8	22.5
	POTENTIAL ORE	
Aroostock County, Maine	313.6	9
Cuyuna Range, Minn.	504.0	5
Chamberlain, S. Dak.	77.3	15.5
Artillery Peak, Ariz.	174.7	4
Leadville, Colo.	4.0	15
Three Kids, Nev.	5.0	10
Pioche, Nev.	4.0	10

APPENDIX

TABLE 7

U.S. CAPACITY FOR STEEL PRODUCTION, JAN. 1, 1960[53]

State	Electric Furnace		Blast Furnace		Open-Hearth Furnace		Basic Oxygen Steel Furnace	
	No. of Plants/ Furnaces	Annual Capacity (net tons)	No. of Plants/ Furnaces	Annual Capacity (net tons)	No. of Plants/ Furnaces	Annual Capacity (net tons)	No. of Plants/ Furnaces	Annual Capacity (net tons)
Ohio	8/36	3,078,600	22/52	18,734,500	17/169	22,688,280		
Pennsylvania	31/105	2,888,780	23/76	26,381,750	30/283	34,944,350	1/2	880,000
Illinois	8/28	2,400,400	6/22	7,955,200	6/62	9,842,000	1/2	452,000
Michigan	4/20	1,178,600	3/9	5,290,250	2/27	5,420,000	1/5	1,385,400
Texas	5/12	699,080	2/2	925,000	2/13	1,825,000		
Alabama	4/8	670,020	7/22	5,817,440	3/31	4,786,000		
California	3/8	628,000	1/4	1,997,800	6/30	2,727,500	1/3	1,440,000
Kentucky	2/5	466,190	1/3	1,058,000	2/15	1,363,000		
Missouri	1/2	420,000			1/4	420,000		
Washington	3/6	401,000						
Georgia	1/2	325,000						
New York	6/28	225,010	6/17	5,947,000	3/47	7,195,000		
Maryland	2/11	180,960	1/10	5,480,000	1/35	7,864,000		
Oregon	1/3	150,000						
Oklahoma	1/1	140,000						
West Virginia	1/1	117,000	2/5	2,646,000	1/14	3,300,000		
Indiana	2/7	101,500	3/23	10,324,350	4/120	18,339,000		
Connecticut	1/2	84,000						
Arizona	1/2	60,000						
Florida	1/1	51,000						
Mississippi	1/1	45,000						
Virginia	2/4	40,000	1/2	128,000				
Tennessee	1/2	38,000	2/3	217,740				
New Jersey	1/6	7,800						
Colorado					1/9	235,000		
Minnesota			1/4	922,400	1/17	1,800,000		
Massachusetts			2/3	696,000	1/9	973,000		
Utah			1/1	195,000				
Rhode Island			2/5	1,804,200	1/10	2,300,000		
Delaware					1/4	93,000		
					1/7	506,500		
Total	91/301	14,395,940	86/263	96,520,630*	84/906	126,621,630	4/12	4,157,400

*Includes 877,500 tons ferroalloys capacity.

APPENDIX

TABLE 8

PRODUCERS OF FERROALLOYS IN THE UNITED STATES IN 1966 [45]

Producer	Plant Location	Product*	Type of Furnace
The Anaconda Company	Anaconda, Fla.	FeMn	Electric
Bethlehem Steel Co.	Johnstown, Pa.	FeMn	Blast
Chromium Mining and Smelting Corp.	Woodstock, Tenn.	FeMn, SiMn	Electric
Interlake Steel Corp.	Beverly, Ohio	SiMn	Electric
E. J. Lavino & Co.	Sheridan, Pa. Reusens, Va.	FeMn FeMn	Blast Blast
Manganese Chemicals Corp.	Kingwood, W. Va.	FeMn	Electric
The New Jersey Zinc Co.	Palmerton, Pa.	Spln	Electric
Ohio Ferro-Alloys Corp.	Philo, Ohio	FeMn, SiMn	Electric
Pittsburgh Metallurgical Company	Niagara Falls, N. Y.	SiMn	Electric
Tenn-Tex Alloy & Chemical Corp.	Houston, Tex.	FeMn, SiMn	Electric
Union Carbide Corp., Mining & Metals Div.	Alloy, W. Va. Marietta, Ohio Ashtabula, Ohio Sheffield, Ala. Portland, Oreg. Rockwood, Tenn.	FeMn, SiMn FeMn, SiMn FeMn, SiMn FeMn FeMn, SiMn FeMn, SiMn	Electric Electric Electric Electric Electric Electric
United States Steel Corp.	Birmingham, Ala. Clairton, Pa. Duquesne, Pa.	FeMn FeMn FeMn	Blast Blast Blast
Vanadium Corp. of America	Graham, W. Va.	FeMn	Electric

*FeMn, ferromanganese; Spln, spiegeleisen; SiMn, silicomanganese.

APPENDIX

TABLE 9

MANGANESE EMISSIONS FROM METALLURGICAL FURNACES [55]

Furnace	Manganese in Particulate (Percent)	Dust Emission Rate pounds dust/ton ore		Manganese Emission Rate pounds/ton ore	
		No Control	Control	No Control	Control
Ferromanganese blast furnace	15-25	360	60	54-90	9-15
Open-hearth furnace	0.6 (MnO)	9.3	1.7	0.056	0.01
Electric-arc steel furnace*	4 (MnO)	11	1.2	0.44	0.044
Basic oxygen furnace	4.4 (Mn_3O_4)	20-40	0.2-0.4	0.88-1.76	0.0088-0.0176

*These emissions are based on the production of steel. When electric-arc furnaces produce ferromanganese, the manganese concentration may be higher.

APPENDIX

TABLE 10

MANGANESE EMISSIONS FROM COAL-FIRED POWER PLANTS[31]

Type of Boiler	$\mu g/m^3$ Before Fly-ash Collection	$\mu g/m^3$ After Fly-ash Collection
Vertical[a]	1,700	60
Corner[c]	970	100
Front-wall[b]	3,900	370
Spreader-stoker[c]	1,400	300
Cyclone-fired unit[b]	1,300	280
Horizontally opposed[c]	2,400	170

[a]Fly-ash collector is cyclone-type separator followed by an electrostatic precipitator.

[b]Fly-ash collector is an electrostatic precipitator.

[c]Fly-ash collector is a cyclone-type separator.

TABLE 11

"ETHYL" ANTIKNOCK COMPOUND-TEL MOTOR 33 MIX[58]

Compound	Weight %
Tetraethyllead	57.5
Methyl cyclopentadienylmanganese tricarbonyl	7.0
Ethylene dibromide	16.7
Ethylene dichloride	17.6
Other (dye, inerts)	1.2

TABLE 12

CONCENTRATION OF MANGANESE IN THE AIR [2,4,6,7]
($\mu g/m^3$)

Location	1954-59		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Alabama												
Birmingham											1.60	.30
Arizona												
Phoenix			.72	.26			.21	.09			.25	.06
California												
Los Angeles	1.86	.27	.11	.05	.11	.04	.19	.07	.08	.03		
San Francisco	.03						.07	.02	.05	.01		
Colorado												
Denver	.20	.05					.16	.08	.45	.08	.09	.04
District of Columbia												
Washington	.16	.05					.14	.05	.08	.03	.06	.03
Georgia												
Atlanta	.30	.09							.36	.08		
Idaho												
Boise			.09	.03			.08	.03			.05	.02
Illinois												
Chicago	.60	.14			.32	.13			.24	.08	.17	.07
Cicero							.34	.10				
East St. Louis	.20	.06							.25	.09		
Indiana												
East Chicago	1.20	.16									1.00	.28
Indianapolis					.35	.10	.27	.07				
Iowa												
Des Moines			.15	.07			.18	.05			.06	.03
Louisiana												
New Orleans	.10	.01					.06	.02				
Maryland												
Baltimore	.33	.09			.52	.14	.72	.10			.49	.10

(continued)

TABLE 12 (Continued)

CONCENTRATION OF MANGANESE IN THE AIR[2,4,6,7]
($\mu g/m^3$)

Location	1954-59		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Massachusetts												
Boston	.03										.05	.0
Michigan												
Detroit	2.64	.69					.45	.10	.42	.12	.74	.2
Missouri												
St. Louis	.30	.05					.42	.10	.13	.05	.22	.0
Montana												
Helena											.07	.0
Nevada												
Las Vegas					.35	.07	.39	.07	.12	.04	.17	.0
New Jersey												
Newark					.48	.05	.14	.05			.09	.0
New York												
Buffalo							.75	.17				
New York	.31	.06			.16	.06	.13	.05	.12	.04	.07	.0
North Carolina												
Charlotte											.31	.0
Ohio												
Cincinnati	9.29	.27	1.80	.37	2.40	.39	2.30	.43	1.30	.16	2.00	.4
Cleveland							1.70	.31	.96	.24	1.00	.1
Pennsylvania												
Allentown					1.20	.33						
Philadelphia	3.86	.05	1.50	.27	9.98	.70	1.30	.25	3.70	.62	1.90	.4
Pittsburgh	.70	.16					1.20	.26	1.40	.27	.82	.2
Scranton					.36	.13						
Tennessee												
Chattanooga	3.00	.32				.59	.21				.37	.1
Texas												
El Paso							.55	.10			1.10	.1

(continued)

TABLE 12 (Continued)

CONCENTRATION OF MANGANESE IN THE AIR [2,4,5,7]
($\mu g/m^3$)

Location	1954-59		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Washington												
Seattle	.24	.07					.29	.05	.09	.03		
Tacoma							.12	.04			.07	.02
West Virginia												
Charleston	1.20	.32			9.98	1.85					9.98	1.33
Wisconsin												
Milwaukee	.25	.05									.47	.12
Wyoming												
Cheyenne											.02	